

The data can be fitted equally well by either Theories I or II of Rice and Ramsperger by using fourteen squared terms.

A table summarizing the present data on unimolecular reactions is given and discussed.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

THE TEMPERATURE COEFFICIENT OF THE THERMAL DECOMPOSITION OF AMMONIA ON PLATINUM

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The heat of activation of the thermal decomposition of ammonia on the surface of a number of metals is about 40,000 to 50,000 calories per mole up to 800°. In particular, Kunsman has found this to be true for tungsten, molybdenum, nickel, iron and supported iron catalysts.² The same value was found for a copper catalyst.³ At pressures below 25 mm. Schwab and Schmidt found 44,000 calories per mole for platinum; but above 25 mm. the value observed was 144,000.⁴ No intermediate values for the heat of activation were observed. Since facilities were at hand it seemed well worth while to confirm or correct this abnormally high temperature coefficient.

Experimental

Experiments were carried out by a dynamic method which has been described.³ The only changes made were in the catalyst and the tube which held the catalyst. A platinum wire gauze was made into a small roll, 6 cm. long, and placed in a fused quartz tube of 10-mm. bore. The platinum wire was 0.010 cm. in diameter and its total apparent surface 310 sq. cm. This catalyst approximates that used by Schwab and Schmidt. The quartz tubing was connected to the rest of the apparatus by means of graded quartz-Pyrex seals. The rate of decomposition of ammonia on this catalyst was determined in the way previously described, with and without added hydrogen or nitrogen, at the temperatures 776, 826 and 858°.

Results

A summary of a number of typical experiments is given in Table I. The first column gives the number of the experiment; the second the barometric pressure in centimeters of mercury; the third, fourth and fifth

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² Kunsman, *THIS JOURNAL*, 50, 2100 (1928); 51, 688 (1929); see also Elöd and Banholzer, *Z. Elektrochem.*, 32, 555 (1926).

³ Dixon, *THIS JOURNAL*, 53, 1763 (1931).

⁴ Schwab and Schmidt, *Z. physik. Chem.*, B3, 337 (1929).

columns give the inlet flow rates of ammonia, nitrogen and hydrogen, respectively, each in cc. per minute reduced to 25° and 760 mm.; the sixth column gives the percentage decomposition in passing through the catalyst tube; the seventh, the temperature in degrees centigrade; and the eighth column gives the velocity constant. The constants were calculated according to the assumption that the rate of decomposition was proportional to the ammonia partial pressure and independent of the pressure of hydrogen and nitrogen. That is

$$k = (v'_N + v'_H + 2v') \ln \frac{v_t^1}{v_t} + v_t - v'$$

where v'_N , v'_H and v' are the inlet flow rates of nitrogen, hydrogen and ammonia, respectively, and v_t is the outlet flow rate of ammonia.⁵ The small changes in barometric pressure were neglected.

TABLE I
THE RATE OF DECOMPOSITION OF AMMONIA ON PLATINUM WIRE

Expt.	Barometric pressure, cm.	Inlet NH ₃ , cc./min.	Inlet N ₂ , cc./min.	Inlet H ₂ , cc./min.	% NH ₃ decomposed	t, °C.	k
33, 35	76.1	40.4	0.0	0.0	21.50	858	10.6
34	76.0	40.4	.0	25.0	13.80	858	10.2
36	76.2	40.4	.0	14.0	16.90	858	10.9
37	76.1	15.5	.0	14.0	14.15	826	4.7
38	76.1	15.5	.0	0.0	22.65	826	4.4
46	75.6	21.9	.0	.0	29.45	858	8.8
47	75.6	21.9	7.3	.0	28.35	859	10.8
48	75.7	43.4	0.0	.0	16.43	858	8.4
52	75.8	43.4	.0	.0	16.83	858	8.7
53	75.8	43.4	.0	60.5	8.86	858	8.9

Apparently the addition of hydrogen has no effect other than that of reducing the ammonia pressure. With nitrogen present, the rate of decomposition is *higher* than expected. Since nitrogen reduces both the partial pressure of the ammonia and that of the hydrogen formed by decomposition, we can explain the increased velocity in the presence of nitrogen by assuming that hydrogen actually inhibits the decomposition process. At low pressures of hydrogen the rate of decomposition is inversely proportional to these pressures, but at high pressures the inhibiting effect reaches a constant value and the reaction proceeds as if it were unimolecular with respect to the ammonia. A calculation shows that when the average hydrogen pressure falls below about 10 cm., the constants, according to Equation 1, begin to increase. In between the low and high pressure regions the hydrogen should inhibit in a way which is intermediate between the two extreme cases.⁵ Over the length of the catalyst each of the three cases may exist, but the constants, such as are given in Table I,

⁵ Hinshelwood, "Kinetics of Chemical Changes in Gaseous Systems," Oxford Press, p. 196.

are sufficiently comparable and accurate to determine the temperature coefficient of the reaction.

The experiments were complicated because of a small amount of decomposition of the ammonia on the quartz tube which held the catalyst. The area of the quartz surface was 78 sq. cm. At the end of the experiments with platinum, the wire gauze was removed, the tube cleaned with aqua regia, the empty tube sealed to the apparatus again and the amount of decomposition determined. The results are given in Table II.

TABLE II
THE DECOMPOSITION OF AMMONIA ON QUARTZ

Expt.	Barometric pressure, cm.	Inlet NH ₃ , cc./min.	% NH ₃ decomposed	<i>t</i> , °C.
1, 4	76.9	43.4	2.58	858
2	76.9	43.4	4.72	902
3	76.9	43.4	1.99	826

If hydrogen inhibits the decomposition on quartz, the values of the percentage decomposition due to quartz in Table II would have been even smaller if the platinum had been present. The figures in Table I have not been corrected for the decomposition on quartz.

Since the catalyst showed a decrease in activity during the course of its entire use, the temperature coefficient has been determined from comparable experiments at different temperatures. Table III shows clearly which experiments have been compared, excepting that the runs with added nitrogen have been omitted. The first column gives the experiments from which the constants in columns two, four and six were calculated. The temperatures of the experiments are given at the top of the table and the ratios of the constants for two successive temperatures are given in columns three and five. The inlet flow rate of ammonia is given in the last column.

TABLE III
TEMPERATURE COEFFICIENT OF THE DECOMPOSITION OF AMMONIA ON PLATINUM WIRE

Expt.	<i>t</i> = 772°C. <i>k</i>	Ratio	<i>t</i> = 826°C. <i>k</i>	Ratio	<i>t</i> = 858°C. <i>k</i>	Inlet NH ₃ , cc./min.
23-30	2.4	2.34	5.6	1.75	9.9	30.4
31-36	2.5	2.72	6.8	1.57	10.6	40.4
37-44			4.6	1.71	7.8	15.5
45-47			5.2	1.70	8.8	21.9
48-53			5.0	1.72	8.6	43.4
Mean		2.53		1.7		

The heat of activation calculated from the temperature coefficient between 772 and 826° is 39,000 calories per mole and between 826 and 858° is 41,000 calories per mole. The average hydrogen pressure increases with the temperature and consequently the calculated temperature coefficients may

be slightly low. The heat of activation which was found by Schwab and Schmidt at low pressures was 44,000 calories; hence the agreement is good.

The fact that the temperature coefficient is nearly the same for all metals seems to indicate that the mechanism of the ammonia decomposition is the same on each metal. Since experiments on different metals have not been carried out under comparable conditions, it is fruitless to attempt to find a relation between the velocity of decomposition and the heat of reaction.

Summary

The decomposition of ammonia on platinum gauze has been studied by a flowing method between 772 and 858°. The rate of decomposition is proportional to the ammonia pressure and inversely proportional to the hydrogen pressure. As the pressure of the hydrogen increases, its inhibiting effect reaches a constant value and the reaction proceeds unimolecularly with respect to the ammonia. The heat of activation of the reaction is 40,000 calories per mole. This value is in agreement with those found for a number of other metals.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

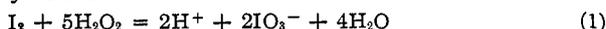
REACTIONS INVOLVING HYDROGEN PEROXIDE, IODINE AND IODATE ION. IV. THE OXIDATION OF IODINE TO IODATE ION BY HYDROGEN PEROXIDE¹

BY HERMAN A. LIEBHAFSKY

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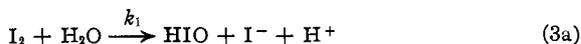
A preliminary study of the reaction



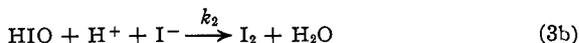
has led Bray and Caulkins (II) to conclude from the rate law

$$-\frac{d\text{I}_2}{dt} = k(\text{I}_2) \quad (2)$$

which it obeys in a rather large region of concentrations, that its principal rate-determining steps are the reactions



and



which taken together constitute the hydrolysis equilibrium of iodine. They found reasonable agreement between their value of k ($k = 0.6$ at 25°) and the value of the specific rate for the iodine hydrolysis ($k_1 = 0.25$ at

¹ The earlier papers of this series are (a) Bray and Liebhafsky, *THIS JOURNAL*, 53, 38 (1931); (b) Bray and Caulkins, *ibid.*, 53, 44 (1931); (c) Liebhafsky, *ibid.*, 53, 896 (1931).